

**HIGH PRODUCTION VOLUME (HPV)  
CHEMICAL CHALLENGE PROGRAM**

**FINAL DATA SUMMARY**

for

**TALL OIL  
AND  
RELATED SUBSTANCES**

CAS No. 8002-26-4  
CAS No. 8016-81-7  
CAS No. 68140-16-9  
CAS No. 68152-92-1  
CAS No. 65997-01-5  
CAS No. 68647-71-2  
CAS No. 65997-02-6

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**By**

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# Final Data Summary for Tall Oil and Related Substances

## Summary

As part of the High Production Volume (HPV) Program, the Pine Chemicals Association, Inc. (PCA) has sponsored seven HPV chemicals. This final summary addresses the following seven chemicals, known collectively as Tall Oil and Related Substances:

8002-26-4, Tall Oil  
8016-81-7, Tall Oil Pitch  
68140-16-9, Tall Oil Pitch, sodium salt  
68152-92-1, Tall Oil, disproportionated  
65997-01-5, Tall Oil, sodium salt  
68647-71-2, Tall Oil, potassium salt  
65997-02-6, Wastewater, tall oil soap acidulation

This summary encompasses data previously described in the Test Plan for these substances as well as newly acquired data. The totality of the data shows that these chemicals are all non-toxic.

These seven substances are all derived from or closely related to tall oil, a by-product from the pulping of pine trees. Tall oil and the various derivatives in this group are all complex mixtures (Class 2 substances). They are composed of numerous chemicals -- the most common of which are rosin and fatty acids, with lesser amounts of terpenes and sterols. Each species of pine tree yields a somewhat different mix of tall oil, and even within a species, the composition of the tall oil could be influenced by the climate and local terrain. However, all the members of this group are similar in chemical composition, being predominantly the extractives that remain after the pulping of wood. Thus, PCA elected to treat these chemicals as a category for purposes of the HPV program, and EPA agreed with this approach.

Where applicable, PCA conducted physical/chemical property and environmental fate testing on all of these substances. With respect to toxicological testing, available data showed that tall oil is non-toxic in acute studies. For the other SIDS health effects endpoints, including repeat dose, reproductive, developmental, ecotoxicity and *in vitro* genotoxicity testing, PCA tested a representative substance from the category.

Tall oil is the source of most of the substances in this category, except acidulation wastewater (which is essentially wastewater containing about 1 - 2 % tall oil). Tall oil is used as the feedstock for fractional distillation, from which a variety of useful fractions (rosin, fatty acids, distilled tall oil, heads and pitch) are derived.

Tall oil pitch (the residue after other fractions are distilled away) is primarily consumed as fuel by the tall oil processor; small amounts are converted to salts for

use in the asphalt industry. Tall oil salts are used in the production of soaps and detergents, and in metal working fluids. Disproportionated tall oil is used in the rubber industry as a processing aid.

Tall oil (CAS# 8002-26-4) (which includes crude and distilled tall oil) was selected as the representative of this category for testing purposes because it is commercially the most important member of the category. It is the source of most of the substances in this category and the others are associated with its production. All the substances in the tall oil category are similar in chemical composition, being predominantly tall oil or its salts. In addition, tall oil is the source of almost all of the 36 substances included in the entire PCA HPV program. Distilled tall oil was used as the representative substance in this group for testing for the applicable SIDS ecotoxicity and mammalian toxicity tests because it is more uniform in composition and physical state than crude tall oil. In addition, products based on distilled tall oil are far more common than those based on crude tall oil, which is used almost exclusively as a distillation feed.

The totality of the SIDS data for the substances in this category is briefly summarized below and in Tables 1-3. As shown in these summaries, tall oil and related substances are all non-toxic in both mammalian and aquatic test systems. These data are described and discussed in the main document. Detailed Robust Summaries of all relevant data are appended to this document.

### **Physical/Chemical Properties**

The SIDS physical and chemical properties were determined when appropriate; however, many of these endpoints are either inapplicable or cannot be measured for these compounds.

- Melting or boiling points were not determined because these substances will either not give a sharp melting point when heated or will decompose before they melt or boil.
- Under ambient conditions, the vapor pressure of these chemicals is essentially zero and experimental measurement is not possible.
- Water solubility and partition coefficients are summarized in Table 1. It should be noted that although all of the non-salt substances in this category are essentially insoluble in water, considerable effort was undertaken to accurately determine water solubility.
- With respect to the partition coefficient ( $K_{ow}$ ), the approved method (OECD 117) yields a range of values rather than a single value representative of the mixture. The range of values reflects the partition coefficients of the individual constituents of these complex mixtures.

The details on these test results are provided in the Robust Summaries.

**Table 1. Summary of Physical/Chemical and Environmental Fate Data\***

| Chemical Name & CAS #                 | Required SIDS Endpoint |                       |                           |
|---------------------------------------|------------------------|-----------------------|---------------------------|
|                                       | Partition Coefficient  | Water Solubility Mg/l | Biodegradation At 28 days |
| Tall oil                              | 4.9-7.7                | 9                     | 56 - 84% <sup>a</sup>     |
| Tall oil pitch                        | 3.3-6.1                | LM                    | 41%                       |
| Tall oil pitch, sodium salt           | 5.8                    | Miscible              | 67%                       |
| Tall oil, disproportionated           | 4.4-5.9                | 11                    | 47%                       |
| Tall oil, sodium salt                 | 4.9-7.6                | Miscible              | 78%                       |
| Tall oil, potassium salt              | 4.9-7.6                | Miscible              | 78%                       |
| Wastewater, tall oil soap acidulation | NM                     | NM                    | NM                        |

a These values represent the results from three different tests; see Robust Summaries for details; LM=lack of analytical method, see summary document for details; NM=not measured, see summary document for details.

\*No testing was conducted for melting point, boiling point, vapor pressure, hydrolysis, photodegradation, and transport and distribution between environmental compartments as explained in summary document.

## Environmental Fate

The SIDS environmental fate endpoints were determined where appropriate; however, many of these endpoints are either inapplicable or cannot be measured for these compounds.

- Photodegradation was not relevant, since the vapor pressure of these compounds is essentially zero and they could not enter the atmosphere.
- Hydrolysis in water was not determined for any of the compounds in this category because all have low water solubility and also lack a functional group that would be susceptible to hydrolysis.
- Transport and distribution between environmental compartments (i.e., fugacity) was not determined due to the inability to provide usable inputs to the required model.
- Biodegradation data are summarized in Table 1 and show that these substances are substantially biodegradable in the environment.

The details on these test results are provided in the Robust Summaries.

## Ecotoxicity

Tall oil was tested for acute toxicity to fish, daphnia and algae at the maximum measured water solubility. These data are summarized in Table 2 and show that none of the compounds in this category are toxic to algae, daphnia or fish. The details of these test results are provided in the Robust Summaries.

**Table 2. Summary of Ecotoxicity Data**

| Chemical Name                           | Required SIDS Endpoint                |   |  |
|---|---------------------------------------|---|--|
|   | Acute Fish<br>96 hr NOEL <sub>r</sub> | Acute<br>Daphnia<br>48 hr NOEL <sub>r</sub> | Acute Algae<br>72 hr NOEL <sub>r</sub> |
| Tall-oil                                | 1000 mg/l                             | 1000 mg/l                                   | 1000 mg/l                              |
| Tall oil pitch                          | C                                     | C   | C                                      |
| Tall oil pitch, sodium salt             | C                                     | C   | C                                      |
| Tall oil, disproportioned               | C                                     | C   | C                                      |
| Tall oil, sodium salt                   | C                                     | C   | C                                      |
| Tall oil, potassium salt                | C                                     | C   | C                                      |
| Waste water, tall oil, soap acidulation | C                                     | C   | C                                      |

C = Indicates category read-down from available data  
 NOEL<sub>r</sub> = no observed effect loading rate

### Mammalian Toxicity

For the SIDS human health endpoints, there were sufficient data on acute toxicity for tall oil demonstrating that this compound is non-toxic. Tall oil was tested for repeat dose toxicity, reproductive and developmental toxicity using OECD 422, as well as *in vitro* genotoxicity testing for mutations in *Salmonella* (Ames test) (OECD 471) and *in vitro* for chromosomal aberrations (OECD 473) in Chinese hamster ovary cells both with and without metabolic activation. The LD<sub>50</sub> for tall oil pitch was > 2000 mg/kg. The mammalian toxicity data are summarized in Table 3 and demonstrate that tall oil is non-toxic. Based on the category approach, results for the test substance also represent other members of the category. The details of these test results are provided in the Robust Summaries.

**Table 3. Summary of Mammalian Toxicity Data**

| Chemical Name                         | Required SIDS Endpoints       |                    |                             |             |  |
|---------------------------------------|-------------------------------|--------------------|-----------------------------|-------------|--|
|                                       | Acute Oral                    | Repeat Dose        | In vitro genetox (Mutation) |             | Repro/ Develop   |
| Tall oil                              | LD <sub>50</sub> > 5000 mg/kg | NOEL = 100 mg/kg/d | +S9<br>Neg.                 | -S9<br>Neg. | +S9<br>-S9<br>Clastogenic only at overtly toxic concentrations with S9 |
| Tall oil pitch                        | LD <sub>50</sub> > 2000 mg/kg | C                  | C                           | C           | C  |
| Tall oil pitch, sodium salt           | C                             | C                  | C                           | C           | C  |
| Tall oil, disproportioned             | C                             | C                  | C                           | C           | C  |
| Tall oil, sodium salt                 | C                             | C                  | C                           | C           | C  |
| Tall oil, potassium salt              | C                             | C                  | C                           | C           | C  |
| Wastewater, tall oil soap acidulation | C                             | C                  | C                           | C           | C  |

C = Indicates category read-down from available data.

## Overall Hazard Evaluation and Potential Exposure

For potential human health effects, the totality of the SIDS data demonstrate that tall oil is non-toxic. Accordingly, based on the category approach, it can be inferred that all of the substances in this group are also non-toxic.

Tall oil has no acute oral toxicity (i.e.,  $LD_{50} > 2,000$  mg/kg), and repeat dose toxicity data demonstrate a no observed effect level (NOEL) of approximately 100 mg/kg/day and a NOEL of approximately 500 mg/kg/day for reproductive/developmental effects. The lack of acute oral toxicity (i.e.,  $LD_{50} > 2,000$  mg/kg) for tall oil pitch is confirmatory of the lack of acute toxicity of the substances in this category. *In vitro* genotoxicity test results show no evidence of mutagenicity in *Salmonella* (i.e., Ames test) for tall oil. Chromosomal aberrations in Chinese hamster ovary (CHO) cells were evident only in the presence of metabolic activation with concentrations of tall oil that were overtly toxic to the cells.

Consequently, no adverse health consequences would be associated with any exposures to tall oil or related substances. For potential ecotoxicological effects, the data on tall oil demonstrate that all of the substances in this category are non-toxic to aquatic organisms including fish, daphnia and algae with the  $NOEL_r$  for each test  $> 1000$  mg/l.

With respect to potential exposure to the substances in this category, all are consumed almost entirely as industrial intermediates where they are reacted or further distilled to produce other chemicals. Of the various tall oil products, it is estimated that greater than 95% are consumed as intermediates in the production of the wide array of products derived from tall oil. Volatilization to air and hence inhalation exposure would be minimal due to the essential lack of a vapor pressure for these substances. Exposure in all of these industrial applications is generally limited to dermal contact during manufacture of the numerous products derived from tall oil and related substances.

The Pine Chemicals Association, Inc. HPV Task Force includes the following companies:

Akzo Nobel Resins  
Akzo Nobel - Eka Chemicals Incorporated  
Arizona Chemical Company  
Asphalt Emulsion Manufacturers Association  
Boise Cascade Corporation  
Cognis Corporation  
Eastman Chemical Co. (including the former Hercules Inc. Resins Division)  
Georgia-Pacific Resins Inc.  
Hercules Inc.  
ICI Americas (including the former Uniqema)  
Inland Paperboard & Packaging, Inc.  
International Paper Co. (including the former Champion International Corporation)  
Koch Materials Co.  
McConnaughay Technologies, Inc.  
Mead Westvaco (includes the former Westvaco)  
Packaging Corporation of America  
Plasmine Technology, Inc.  
Raisio Chemicals  
Rayonier  
Riverwood International  
Smurfit – Stone Container Corporation  
Weyerhaeuser Co.

The PCA HPV Task Force has filed multiple test plans covering various chemicals.  
Not all members of the Task Force produce the substances covered by this test plan.



## I. Description of Tall Oil and Related Substances

The Pine Chemicals Association, Inc. (PCA) has sponsored seven HPV chemicals known collectively as Tall Oil and Related Substances. The Test Plan for this group of substances was posted on EPA's HPV website on July 17, 2001, with comments from the Physicians Committee for Responsible Medicine (PCRM), Environmental Defense (ED) and EPA posted on November 28, 2001, November 30, 2001 and January 10, 2002, respectively. After reviewing these comments, PCA prepared a response which was subsequently posted on EPA's HPV website on June 21, 2002.

This group of chemicals consists of the following:

8002-26-4, Tall Oil  
8016-81-7, Tall Oil Pitch  
68140-16-9, Tall Oil Pitch, sodium salt  
68152-92-1, Tall Oil, disproportionated  
65997-01-5, Tall Oil, sodium salt  
68647-71-2, Tall Oil, potassium salt  
65997-02-6, Wastewater, tall oil soap acidulation

All of the chemicals in this group are closely related to tall oil, which is a by-product from the alkaline pulping of wood, especially pinewood. The precursors of tall oil in the tree are the so-called extractives that make up about 1% of the weight of the wood. These extractives are composed of numerous chemicals, the most common of which are rosin and fatty acids, with lesser amounts of terpenes and sterols. The extractives dissolve in the pulping liquor and are recovered from the liquor when it is concentrated and skimmed. The skimmed material is called tall oil soap and is the sodium salt of tall oil (CAS# 65997-01-5).

Tall oil soap is then acidulated with sulfuric acid to yield crude tall oil (CAS# 8002-26-4). A by-product of this acidulation is "wastewater, tall oil soap acidulation" (CAS# 65997-02-6), which is essentially a solution of sodium sulfate containing dilute amounts of tall oil. Commercially, crude tall oil is fractionally distilled to manufacture tall oil fatty acids and tall oil rosin. These important substances are the key members in other categories of HPV chemicals being sponsored by the Pine Chemicals Association, Inc. A fraction from the distillation process is distilled tall oil, which has the same CAS registry number as crude tall oil.

The other members of this HPV category are all closely related to tall oil. Disproportionated tall oil (CAS# 68152-92-1) is tall oil that has been stabilized to prevent oxidation. Tall oil pitch (CAS# 8016-81-7) is the residue remaining when the tall oil fatty acids and the tall oil rosin have been distilled away. Its main use is for its fuel value. Zinkel and Russell (1989) noted that use of a material similar to tall oil pitch dates back to biblical times. In Genesis 6:14, Noah was instructed to "*pitch the ark within and without,*" indicating the historical use of pine tree resins. The remaining members of the group are simple salts of either tall oil or pitch.

As complex mixtures, tall oil and its derivatives are all considered Class 2 substances.<sup>1</sup> Information on their composition, uses and the challenges of chemical analysis of these complex mixtures is described below.

### A. Composition

All the members of this category are chemically complex, with their composition dependent on the source of the trees from which they were derived and the conditions under which the tall oil was distilled. Consequently, they are not described in terms of their chemical composition, but only in general terms such as their acid number or their overall fatty acid or resin acid content (Zinkel and Russell 1989). However, some general information on the typical composition of each of the seven substances in this category is provided below.

#### 1. Tall Oil (CAS# 8002-26-4)

The TSCA Inventory describes tall oil as, *"A complex combination of tall oil rosin and fatty acids derived from acidulation of crude tall oil soap and including that which is further refined. Contains at least 10% rosin."* The two chief types of tall oil covered by this description are crude tall oil and distilled tall oil. The composition of a typical crude tall oil and a typical distilled tall oil produced in the southeastern U.S. are given in Table 4.

**Table 4**  
**Composition of Typical Tall Oils**

|                           | <b>Crude Tall Oil</b> | <b>Distilled Tall Oil</b> |
|---------------------------|-----------------------|---------------------------|
| Acid number               | 165                   | 185                       |
| Fatty acids (%)           | 52                    | 65                        |
| Resin acids (%)           | 40                    | 30                        |
| Unsaponifiable matter (%) | 8                     | 5                         |

The actual composition of both types of tall oil can vary widely. The composition of crude tall oil depends on the species of tree from which it was derived, while the composition of distilled tall oil depends upon the species of tree as well as the

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<sup>1</sup> As defined in the TSCA Inventory, *"In terms of composition, some chemical substances are single compounds composed of molecules with particular atoms arranged in a definite known structure. For purposes of this discussion, such substances will be denoted Class 1 substances. Many commercial chemical substances are not in this class. They may have variable compositions or be composed of a complex combination of different molecules. These substances will be denoted Class 2 substances."*

processing conditions under which it was manufactured. More detailed information on the composition of the distilled tall oil that was tested for the HPV endpoints is provided in Table 5. The structures of some representative resin acids are shown in Figure 1.

**Table 5**  
**Composition of Distilled Tall Oil Tested**

|  |  |     |
|--|--|-----|
| Palmitic acid                          | $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$   | 3%  |
| Palmitoleic acid <sup>a</sup>          | $\text{CH}_3(\text{CH}_2)_x\text{CH}=\text{CH}(\text{CH}_2)_y\text{COOH}$                                | 1%  |
| Stearic acid                           | $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$   | 1%  |
| Oleic acid                             | $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$                                | 28% |
| Linoleic acid                          | $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CH}-\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ | 19% |
| Linoleic acid, conjugated <sup>b</sup> | $\text{CH}_3(\text{CH}_2)_x\text{CH}=\text{CHCH}=\text{CH}-(\text{CH}_2)_y\text{COOH}$                   | 9%  |
| Other fatty acids <sup>c</sup>         |  | 7%  |
| Isopimaric acid                        | See Fig. 1   | 3%  |
| Abietic acid                           | See Fig. 1   | 10% |
| Dehydroabietic acid                    | See Fig. 1   | 5%  |
| Other resin acids                      |  | 11% |

a:  $x + y = 12$

b: x usually 4 or 5; y usually 7 or 8; but  $x + y = 12$

c: 5,9,12-octadecatrienoic acid; linolenic acid; 5,11,14-eicosatrenoic acid; cis,cis-5,9-octadecadienoic acid; eicosadienoic acid; elaidic acid; cis-11 octadecanoic acid; C-20, C-22, C-24 saturated acids.

## 2. Tall Oil Pitch (CAS# 8016- 81-7)

Tall oil pitch is a tarry semi-solid material with a composition very dependent on the processing conditions under which it was produced. As a consequence of its low acid number, its complex composition and its physical form, most of the pitch produced is consumed for its fuel value.

The TSCA Inventory defines tall oil pitch as *"the residue from the distillation of tall oil. It contains primarily high boiling esters of fatty acids and rosin. It may also contain neutral materials, free fatty acids and resin acids"*. Pitch is primarily made up of high boiling, high molecular weight compounds formed at the high temperatures encountered during the fractionation process. These compounds include the esters of fatty acids and rosin, and small amounts of dimers and trimers of resin acids and fatty acids. Because pitch has such an extremely complex and variable composition, chemical analysis is not feasible, and no typical composition can be presented.

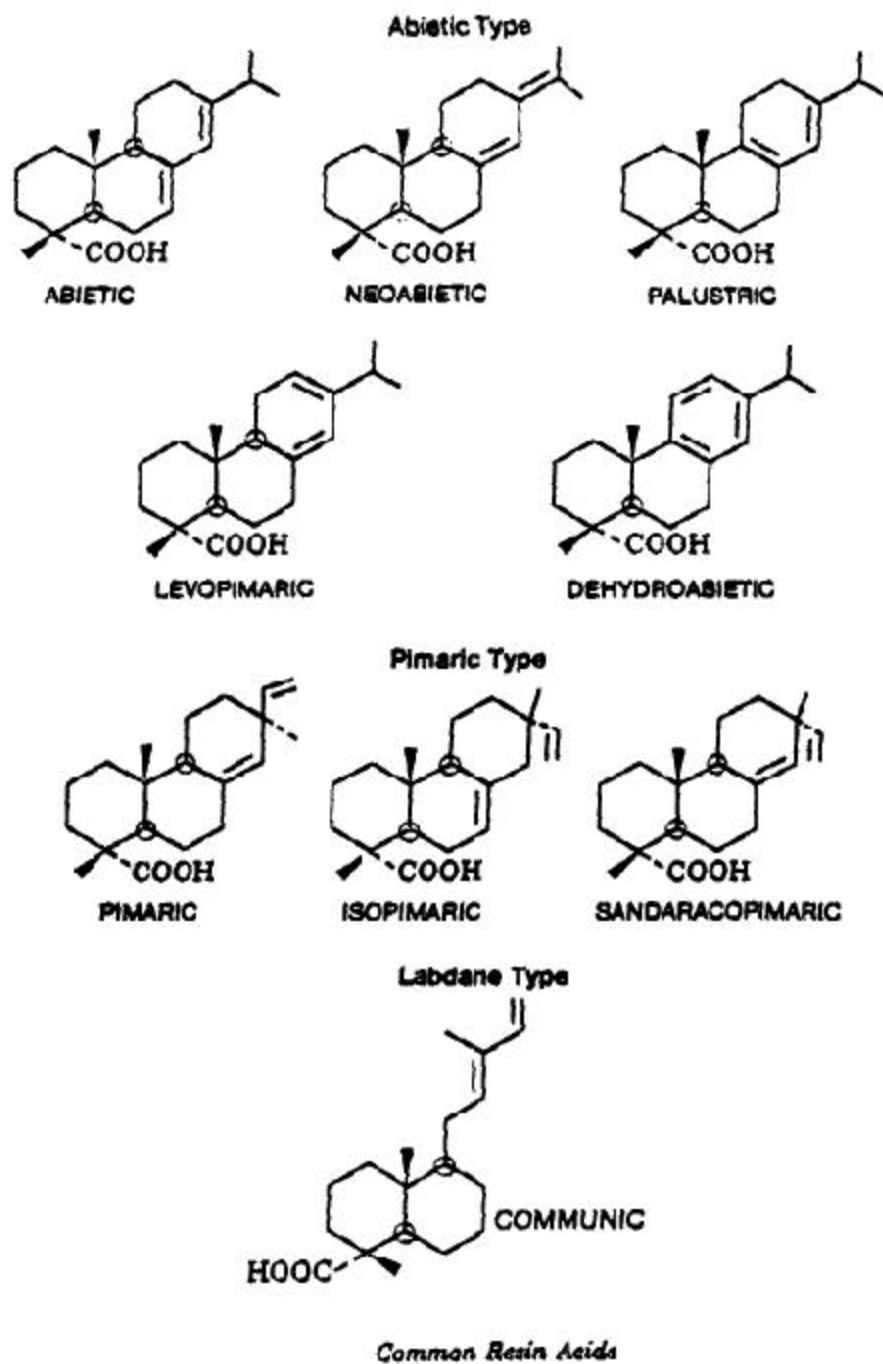


Figure 1. Structures of some representative resin acids found in distilled tall oil and its derivatives.

### **3. Tall Oil Pitch, Sodium Salt (CAS# 68140-16-9)**

This substance is made by neutralizing tall oil pitch with sodium hydroxide. It is sold as an aqueous dispersion.

### **4. Tall Oil, Disproportionated (CAS# 68152-92-1)**

Disproportionated tall oil is distilled tall oil that has been heated with a catalyst that removes conjugated double bonds. The fatty acid and resin acid contents of the treated product are the same as the starting distilled tall oil (see Table 4), but some of the individual components are changed (see Table 6 below). For example, abietic acid is converted to dehydroabietic acid and linoleic acid is converted to oleic acid.

### **5. Tall Oil, Sodium Salt (CAS # 65997-01-5) and Potassium Salt (CAS # 68647-71-2)**

The sodium salt of crude tall oil is also known as tall oil soap, the precursor to tall oil. Both the sodium and potassium salts of tall oil are also produced from distilled tall oil. The salts are made by treating tall oil with the appropriate base and dispersing the salt formed in water. These compounds, as the salts of a strong base and a weak acid, result in alkaline dispersions with the pH dependent on the salt concentration in the dispersion.

### **4. Wastewater, Tall Oil Soap Acidulation (CAS # 65997-02-6)**

The TSCA Inventory defines this byproduct as, *"The aqueous layer formed by acidulation of tall oil soap with sulfuric acid during the production of tall oil. Composed primarily of a solution of sodium sulfate, the remainder being lignin and tall oil."* Typically, tall oil soap acidulation wastewater is about a 12% solution of sodium sulfate, containing about 1 to 2% tall oil. This material has no commercial value except as a minor source of sodium for a kraft pulp mill. When that outlet is not available, the wastewater is typically discharged into a mill's wastewater treatment system.

No testing was undertaken for this material. The Pine Chemicals Association, Inc. (PCA) and the American Forest & Paper Association (AF&PA) petitioned the EPA to remove this byproduct from the HPV list on the grounds that it is an inorganic byproduct and should not be on the list. EPA suggested instead that this material should be treated as "dilute tall oil" since it contains some minor amount of tall oil and did not require independent testing.

## **B. Commercial Uses of Tall Oil and Related Substances**

Tall oil is by far the most important member of this category from a commercial standpoint. The main use of tall oil is as a feedstock to the fractionation process, where tall oil is separated into its various fractions (rosin, fatty acids, distilled tall oil, heads, pitch).

Tall oil pitch, a tarry substance, is mainly consumed as fuel by the tall oil processor.

Tall oil pitch, sodium salt is used in the asphalt industry as a bonding agent in paving applications, or as a plasticizer in asphalt coatings.

Tall oil, disproportionated is important in the copolymerization of styrene and butadiene to produce rubber (SBR) and it is also used in the production of neoprene.

Tall oil, sodium and potassium salts are used in the production of soaps and detergents, as well as in metalworking fluids and lubricants.

Tall oil soap acidulation wastewater is composed of dilute tall oil and is of no commercial value. It is either recycled to the pulping process for the relatively small sodium value or is routed to the producer's wastewater treatment system.

Additional information concerning uses, production and potential exposures to the chemicals in this category are described in greater detail below in the section on *Potential Exposure to Tall Oil and Related Substances*

## **C. Complexity of Analytical Methodology**

All of the substances in this category are Class 2 substances. This, combined with the fact that tall oil is essentially insoluble in water and decomposes on heating at high temperature, creates a variety of analytical issues. Gas chromatography of methylated derivatives was the method used for the analysis of the members of this category. Because the solubility of tall oil is very low (about 10 ppm) the reliability of the standard analytical method was verified at such low concentrations. In spite of intensive efforts to develop an analytical method for pitch, analysis has proved to be infeasible due to the complexity of this material.

## **II. Rationale for Selection of Representative Compound for Testing**

Tall oil (CAS# 8002-26-4) (which includes crude and distilled tall oil) was selected as the representative of this category for testing purposes because it is commercially the most important member of the category and the source of most of the substances in this category and the others are associated with its production. In addition, tall oil is the source of almost all of the 36 substances included in the entire PCA HPV program.

All the substances in this category are similar in chemical composition, being predominantly tall oil or its salts. Distilled tall oil was used as the representative substance in this group for testing for the applicable SIDS ecotoxicity and mammalian toxicity tests because it is more uniform in composition and physical state than crude tall oil. In addition, products based on distilled tall oil are far more common than those based on crude tall oil, which is used almost exclusively as a distillation feed.

Another criterion listed by EPA for grouping chemicals into a category is the use of the "family approach" of examining related chemicals when they are acids or acid salts. Although the salts of tall oil and tall oil pitch have different physical characteristics, they are included in this group because they are quickly converted into the free tall oil or tall oil pitch when they are treated by acid or by dilution, as they would be under typical toxicity testing conditions. In summary, this category of chemicals fits the requirements of the EPA's HPV Challenge program for a chemical category, and distilled tall oil was the most appropriate representative test material from this category.

After reviewing the *Test Plan for Tall Oil and Related Substances*, EPA while agreeing with the overall proposed category, suggested that PCA consider whether tall oil pitch (CAS # 8016-81-7), pitch salt (CAS # 68140-16-9), and disproportionated tall oil (CAS # 68152-92-1) should also be tested. The Agency questioned whether test results for tall oil would be representative of these substances because their compositions may be significantly different. Environmental Defense (ED) also suggested testing tall oil pitch due to potential differences in composition.

After carefully considering these comments, PCA concluded that the representative compound for testing would remain as originally proposed based upon the explanation provided in the test plan and the additional reasoning provided below. However, PCA did undertake an additional acute test (OECD 425, the up-down procedure) on tall oil pitch in order to demonstrate that pitch and pitch salt can be represented by the results from the testing of tall oil.

The Agency recommended that PCA consider testing disproportionated tall oil because it was concerned that the process of catalytic conversion of the conjugated double bonds during production might result in a significant change in the chemical composition of the fatty acids relative to the original distilled tall oil. However, as illustrated in Table 6 below, the chemical composition of disproportionated tall oil is similar to distilled tall oil (the representative test substance).

Because these two substances are comprised of the same constituents at varying ratios, there is no reason to believe that these different ratios would affect potential toxicity. Thus, the toxicity of disproportionated tall oil should be similar to distilled tall oil with the test results on distilled tall oil representative of disproportionated tall oil.

**Table 6**  
**Composition of Distilled Tall Oil and Disproportionated Tall Oil**

| <b>Component</b>    | <b>Distilled Tall Oil<br/>(% composition)</b> | <b>Disproportionated<br/>Tall Oil<br/>(% composition)</b> |
|---------------------|---|---|
| Palmitic            | 3   | 3   |
| Stearic             | 1   | 2   |
| Oleic/elaidic       | 28  | 43  |
| Linoleics           | 28  | 9   |
| Unknown Fatty Acids | 7   | 6   |
| Isopimaric          | 3   | 2   |
| Abietic             | 10  | 1   |
| Dehydroabietic      | 5   | 12  |
| Unknown R Acids     | 11  | 16  |

Similarly, EPA and ED raised concerns that the results of toxicity testing on tall oil might not be representative of tall oil pitch and pitch salt. EPA reasoned that the substances must be substantially different in composition due to the lack of an adequate analytical method to fully characterize tall oil pitch noting that *“This inability to fully characterize the tall oil pitch suggests that substantive changes may have occurred in the processing.”*

Pitch is an extremely complex material as its components are either formed during the high temperature (i.e., > 300°C) distillation of tall oil, another complex material, or are the high boiling components of the original tall oil. Consequently, the composition of pitch can only be expressed in a general way with the major components consisting of fatty acids and rosin acids, esters of fatty acids, dimerized acids, and rosin acids, as well as neutral materials. While available data suggest that the various known components have a very low order of toxicity, as noted above, PCA did undertake an acute toxicity test on tall oil pitch to assess this endpoint, using OECD 425 (the “up-down” procedure) to minimize the number of animals used. As discussed below, this testing clearly demonstrated that tall oil pitch (and by inference its sodium salt) has a similar lack of acute toxicity as does distilled tall oil, the representative test substance.

### **III. Summary of Data**

Distilled tall oil was tested for repeat dose, reproductive and developmental toxicity, *in vitro* genotoxicity in bacterial and mammalian cells as well as ecotoxicity; biodegradation was determined for all substances where data were lacking. In



addition, the solubility and partition coefficients for all of the substances in this category were determined. Table 7 summarizes the results from all of the testing conducted on the substances in this category.

**Table 7**  
**Summary of Data**  
**Tall Oil and Related Substances\***

| Chemical and CAS #                               | Required SIDS Endpoints |                              |                   |                                    |                                     |                                     |             |                 |                             |   |                 |
|--|-------------------------|------------------------------|-------------------|------------------------------------|-------------------------------------|-------------------------------------|-------------|-----------------|-----------------------------|---|-----------------|
|  | Partition Coef.         | Water Sol. Mg/l              | Biodeg. @ 28 days | Acute Fish 96 hr. LL <sub>50</sub> | Acute Daph. 48 hr. EL <sub>50</sub> | Acute Algae 72 hr. EL <sub>50</sub> | Acute oral  | Repeat Dose     | In vitro Genetox (Mutation) | In vitro Genetox (Chrom. ab.)                     | Repro/develop   |
| Tall Oil 8002-26-4                               | 4.9-7.7                 | 9                            | 56-84%            | 1000 mg/l                          | 1000 mg/l                           | 1000 mg/l                           | >5000 mg/kg | NOEL= 100 mg/kg | Neg. ± S9                   | Clasto--genic only at overtly toxic conc. with S9 | NOEL= 500 mg/kg |
| Tall Oil Pitch 8016-81-7                         | 3.3-6.1                 | LM                           | 41%               | C                                  | C                                   | C                                   | >2000 mg/kg | C               | C                           | C   | C               |
| Tall Oil Pitch sodium salt 68140-16-9            | 5.8                     | Miscible in H <sub>2</sub> O | 67%               | C                                  | C                                   | C                                   | C           | C               | C                           | C   | C               |
| Tall Oil disproportionated 68152-92-1            | 4.4-5.9                 | 11                           | 48%               | C                                  | C                                   | C                                   | C           | C               | C                           | C   | C               |
| Tall Oil sodium salt 65997-01-5                  | 4.9-7.6                 | Miscible in H <sub>2</sub> O | 78%               | C                                  | C                                   | C                                   | C           | C               | C                           | C   | C               |
| Tall Oil potassium salt 68647-71-2               | 4.9-7.6                 | Miscible in H <sub>2</sub> O | 78%               | C                                  | C                                   | C                                   | C           | C               | C                           | C   | C               |
| Wastewater, tall oil soap acidulation 65997-02-6 | Not tested              | Not tested                   | Not tested        | C                                  | C                                   | C                                   | C           | C               | C                           | C   | C               |

LM -- Lack of a suitable analytical method precludes testing

C -- Indicates category read-down from test data on tall oil or tall oil pitch.

\* No testing was conducted for melting point, boiling point, vapor pressure, hydrolysis, photodegradation, and transport and distribution between environmental compartments as explained in the summary document.

## A. Physicochemical Data

The basic physicochemical data required in the SIDS battery includes melting point, boiling point, vapor pressure, partition coefficient ( $K_{ow}$ ), and water solubility. Class 2 substances are composed of a complex mixture of substances and are often difficult to characterize. As noted above, tall oil, tall oil pitch, disproportionated tall oil and their various salts are Class 2 substances. Their composition is variable and cannot

be represented by a definite chemical structural diagram. Due to this “complex mixture” characteristic of tall oil and related compounds, some physical property measurements are not appropriate as explained below.

### **1. Melting Point**

Tall oil and the other non-salts in this grouping category are liquids at room temperature; tall oil pitch is a semi-solid. A sharp melting point cannot be obtained for any of these compounds due to the complex nature of these substances. The salts are solids under ambient conditions and heating them to determine the melting point would cause thermal decomposition. Consequently, the melting point was not determined for any of the substance in this category.

### **2. Boiling Point**

All of the non-salt members of this category are produced by high temperature, high vacuum distillation and are non-volatile at ambient temperatures. A boiling point at ambient pressure has no significance because when heated to high temperatures these materials will thermally decompose before they boil. The two salts in this category are solids. When heated to high temperatures, they will also thermally decompose before boiling. Accordingly, measurement of this property was inappropriate for all the substances in this category.

### **3. Vapor Pressure**

Vapor pressures for tall oil and the other chemicals in this category at ambient temperatures are effectively zero, and their experimental measurement is inappropriate. The salt members of the category are solids and thus have no vapor pressure, so this end point cannot be measured. When dissolved in water, their solutions will reflect the vapor pressure of the water rather than the salt, and therefore measurement of this property was inappropriate.

### **4. Water Solubility**

The water solubility of five compounds in this category was determined using OECD protocol (105) with the results shown in Table 8. The values in Table 8 for tall oil and tall oil, disproportionated represent the sum solubility of all the components of the test material. The solubility based on the 3 major components of tall oil (i.e., oleic/elaidic acid, linoleic acid and abietic/ dehydroabietic acid) and tall oil, disproportionated (i.e., oleic acid, elaidic acid and dehydroabietic acid) was 1 mg/l and 3 mg/l, respectively. The lack of a suitable analytical method for tall oil pitch precluded the determination of the water solubility.

**Table 8**

| <b>Chemical</b>             | <b>Water Solubility (mg/l)</b> |
|-----------------------------|--------------------------------|
| Tall oil                    | 9                              |
| Tall oil pitch              | Lack of method                 |
| Tall oil pitch, sodium salt | Miscible in water              |
| Tall oil, disproportionated | 11                             |
| Tall oil, sodium salt       | Miscible in water              |
| Tall oil, potassium salt    | Miscible in water              |

All of these data are presented in detail in the Robust Summaries.

### **5. Partition Coefficient**

The partition coefficient (i.e.,  $K_{ow}$ ) for six compounds in this category were determined. While there were adequate data for tall oil and pitch, both were retested with the other compounds in this category for consistency of results. Because all of these substances are Class 2 mixtures, the procedure (OECD 117) to determine the  $K_{ow}$  often yields a range of  $K_{ow}$  values rather than a single value representative of the mixture. Thus, the results reflect the partition coefficients of the components rather than the mixture. The partition coefficient data are shown below in Table 9:

**Table 9**

| <b>Chemical</b>             | <b>Partition Coefficient (<math>K_{ow}</math>)</b> |
|-----------------------------|--|
| Tall oil                    | 4.9 – 7.7  |
| Tall oil pitch              | 3.3 – 6.1  |
| Tall oil pitch, sodium salt | 5.8  |
| Tall oil, disproportionated | 4.4 – 5.9  |
| Tall oil, sodium salt       | 4.9 – 7.6  |
| Tall oil, potassium salt    | 4.9 – 7.6  |

All of these data are presented in detail in the Robust Summaries.

### **B. Environmental Fate Data**

The fate or behavior of a chemical in the environment is determined by the rates or half-lives for the most important transformation (degradation) processes. The basic environmental fate data covered by the HPV Program includes biodegradation, stability in water (hydrolysis as a function of pH), photodegradation and transport and distribution between environmental compartments (fugacity).

## 1. Biodegradation

Biodegradability provides a measure for the potential of compounds to be degraded by microorganisms. Depending on the nature of the test material, several standard test methods are available to assess potential biodegradability as reflected in the different tests shown in Table 10. For the substances in this category OECD method 302B was used for the salts and OECD method 301B was used for the non-salts. Of the chemicals in this category, tall oil and tall oil pitch had two sets of existing data on the biodegradation endpoint as shown in Table 10. Biodegradation for disproportionated tall oil and the three salts was determined. Existing and new data were generated using different protocols as noted in Table 10 below.

**Table 10**

| <b>Chemical</b>             | <b>Percent Biodegradation</b> | <b>Test Method</b> |
|-----------------------------|-------------------------------|--------------------|
| Tall oil (Test 1)           | 60                            | OECD 301D          |
| Tall oil (Test 2)           | 73                            | OECD 301F          |
| Tall oil pitch (Test 1)     | 41                            | OECD 301D          |
| Tall oil pitch (Test 2)     | 9                             | OECD 301B          |
| Tall oil pitch, sodium salt | 32                            | OECD 301B          |
| Tall oil, disproportionated | 33                            | OECD 301B          |
| Tall oil, sodium salt       | 78                            | OECD 302B          |
| Tall oil, potassium salt    | 78                            | OECD 302B          |

All of these data are presented in greater detail in the Robust Summaries.

## 2. Hydrolysis

Hydrolysis as a function of pH is used to assess the stability of a substance in water. Hydrolysis is a reaction in which a water molecule (or hydroxide ion) substitutes for another atom or group of atoms present in an organic molecule. If there is no group suitable to be displaced, then the organic compound is considered to be resistant to hydrolysis. None of the substances in the tall oil category contains an organic functional group that might be susceptible to this physical degradative mechanism. Therefore, hydrolysis need not be measured.

In addition, low water solubility often limits the ability to determine hydrolysis as a function of pH. All of the tall oil compounds have very low solubility in water. Therefore, these materials are expected to be stable in water and it was unnecessary to attempt to measure the products of hydrolysis. With respect to the various tall oil salts, since they exist in an aqueous medium they hydrolyze (ionize) immediately, but form stable species. Consequently, it was also unnecessary to measure this endpoint for tall oil salts.

### 3. Photodegradation

Due to their low water solubility and lack of any measurable vapor pressure at ambient temperatures, there is no opportunity for any of these chemicals to enter the atmosphere. Thus, photodegradation is irrelevant. In addition, based on the constituents in these complex mixtures, there is no reason to suspect that they would be subject to breakdown by a photodegradative mechanism. Consequently, this endpoint was not determined for any of the substances in this category.

In its comments on the *Test Plan for Tall Oil and Related Substances*, while EPA agreed that PCA's approach on photodegradation was a "*reasonable approach for the mixtures*," they also requested estimated photodegradation data for tall oil, disproportionated tall oil and wastewater acidulation, or for their major constituents. This was based on EPA's belief that many of the components of the mixtures have low water solubilities and moderate Henry's law constants so that volatilization from water may be significant. However, Henry's Law pertains to the relationship between the solubility of a gas in a liquid in comparison to its partial pressure above the liquid. Tall oil is a non volatile viscous liquid composed primarily of oleic acid, linoleic acid and rosin, none of which exist in a gaseous state at ambient temperatures. Consequently, Henry's Law is not relevant to any of the substances in this category since none of them vaporize at ambient temperatures and so there are no vapors to photodegrade.

### 4. Transport and Distribution Between Environmental Compartments

The transport and distribution between environmental compartments (i.e., fugacity) is intended to determine the ability of a chemical to move or partition in the environment. There are various mathematical models for estimating fugacity. One of the most frequently referenced models is the level III model from the Canadian Environment Modeling Centre at Trent University. Even the simplest of these models requires estimates of solubility, vapor pressure and octanol/water partition coefficient to estimate fugacity for a single component. For complex class 2 substances such as tall oil and related substances, estimates of any one of these physical parameters for the various known components would span a range of more than an order of magnitude. When combining three or more parameters of equally variable ranges to derive estimates for different environmental media, the variability in the estimate for any given medium would grow geometrically to more than three or more orders of magnitude. This suggests that any estimates based on arbitrarily selected individual components would be essentially useless for any practical purpose. Add to this the additional fact that there is variability in the chemical composition of these substances (as illustrated in Table 5 and Figure 1 above) and the possible permutations become unmanageable. Consequently, for complex mixtures such as tall oil and related substances, the mathematical models which rely upon estimates for individual components are of no practical use in predicting environmental fate. Therefore, due to the inability to provide usable inputs to the

required model, no determination of transportation and distribution between environmental compartments was undertaken for tall oil and related compounds

In their comments on the *Test Plan for Tall Oil and Related Substances*, EPA recommended that PCA estimate fugacity (transport and distribution between environmental compartments) for the major components of each substance in the tall oil category. Although recognizing that *“parameter values for the individual components are not truly representative of the mixtures in this category, EPA believes that fugacity calculations for the major components of each mixture would prove useful in understanding the environmental behavior of the mixtures.”* However, after considering this suggestion, PCA concluded that such calculations would not be useful for assessing the sponsored chemicals since, as acknowledged by EPA, these calculations are not representative of the sponsored chemicals. PCA’s commitments are to the mixtures themselves as a whole (not the major components) and, thus, PCA determined it was not appropriate to undertake these calculations.

### **C. Ecotoxicity Data**

The basic ecotoxicity data that are part of the HPV Program include acute toxicity to fish, daphnia and algae. While there were existing data on these endpoints for some of the substances in this category, these data are conflicting and it is impossible to determine which, if any, of these findings are representative of ecotoxicity. The inconsistencies in how water samples were prepared for testing these endpoints render these data inadequate. Consequently, acute toxicity to fish, daphnia and alga was retested for tall oil under conditions that maximize the solubility under the specific test exposure conditions, but reduce exposure to insoluble fractions that may cause nonspecific toxicological effects. In addition, the effect of both filtering to further minimize nonspecific physical effects, and of reducing the pH to the lower end of the acceptable range for test organism survival, were also investigated for changes in toxicological effects. The results of preliminary tests were used to select the most appropriate test conditions for the definitive test for each species.

In its comments on the *Test Plan for Tall Oil and Related Substances*, while EPA agreed with the proposed acute toxicity testing of fish, daphnia and algae, it also suggested that PCA conduct a 21-day chronic daphnid reproduction test using a flow-through method with measured concentrations.

After considering this suggestion, PCA determined not to undertake a 21-day chronic daphnid reproduction test. The methodology for preparing the water for the ecotoxicity testing of distilled tall oil was identical to that used to determine the solubility of this substance. This procedure was adopted in order to ensure that ecotoxicity testing was conducted at the limit of actual water solubility. Given the extremely low solubility of the material, the recommendation for a 21-day test using a flow-through method would be impractical due to the amount of water that would be required and the difficulty in performing the necessary serial analytical measurements. In addition, where there is a risk of emulsions forming inherently (as

there might be with tall oil), flow-through testing is not possible and is not recommended pursuant to the OECD (2000) Guidance Document 23 (*Aquatic Toxicity Testing of Difficult Substances and Mixtures*), which EPA specifically recommends PCA should follow. Thus, chronic aquatic toxicity testing in daphnia was not appropriate for this substance.

The ecotoxicity data are summarized in Table 11 below and demonstrate that tall oil is non-toxic to fish, daphnia and algae.

**Table 11**

| <b>Chemical</b> | <b>Fish<br/>96 hr. *NOEL<sub>r</sub></b> | <b>Daphnia<br/>48 hr. NOEL<sub>r</sub></b> | <b>Algae<br/>72 hr. NOEL<sub>r</sub></b> |
|-----------------|--|--|--|
| Tall oil        | 1000 mg/l                                | 1000 mg/l                                  | 1000 mg/l                                |

\*NOEL<sub>r</sub> = No Observed Effect Loading Rate

These data are presented in greater detail in the Robust Summaries.

## **D. Human Health Effects Data**

### **1. Acute Oral Toxicity**

Acute oral toxicity studies investigate the effect(s) of a single exposure to a relatively high dose of a substance. This test is conducted by administering the test material to animals (typically rats or mice) in a single gavage dose. Harmonized EPA testing guidelines (August 1998) set the limit dose for acute oral toxicity studies at 2000 mg/kg body weight. If less than 50 percent mortality is observed at the limit dose, no further testing is needed. A test substance that shows no effects at the limit dose is considered nontoxic. If compound-related mortality is observed, then further testing may be necessary.

### **Summary of Acute Oral Toxicity Data**

Tall oil is non-toxic following acute oral exposure. The acute oral toxicity of tall oil has been determined in two studies in rats. The acute oral LD<sub>50</sub> was > 5000 mg/kg in one study and > 6000 mg/kg in another study. In addition, tall oil pitch was also tested (using the up/down procedure) for acute oral toxicity and the LD<sub>50</sub> was > 2000 mg/kg. Consequently, based on the category approach, it can be concluded that none of the substances in this category would be acutely toxic.

## 2. Repeat Dose Toxicity

Subchronic repeated dose toxicity studies are designed to evaluate the effect(s) of repeated exposure to a chemical over a significant period of the life span of an animal. Typically, the exposure regimen in a subchronic study involves daily exposure (at least 5 consecutive days per week) for a period of not less than 28 days or up to 90 days (i.e., 4 to 13 weeks). The HPV program calls for a repeat dose test of at least 28 days. The dose levels evaluated are lower than the relatively high limit doses used in acute toxicity (i.e., LD<sub>50</sub>) studies, but still substantially higher than potential human exposure levels. In general, repeat dose studies are designed to assess systemic toxicity, but the study protocol can be modified to incorporate evaluation of potential adverse reproductive and/or developmental effects.

### Summary of Repeat Dose Toxicity Data

Tall oil was tested for repeat dose toxicity combined with the test for toxicity to reproduction and developmental toxicity in OECD (422) *Combined Repeated Dose Toxicity Study with the Reproduction/Developmental Toxicity Screening Test*. Four groups of 10 male and 10 female Sprague-Dawley rats received tall oil in the diet at concentrations of 0, 1000, 5000 and 20000 ppm; the approximate doses were 500, 2500 and 10,000 mg/kg. The males were dosed for at least 4 weeks, starting from 2 weeks prior to mating. The females were dosed from 2 weeks prior to mating until at least Day 6 of lactation. The animals were monitored for clinical signs, body weight, food consumption, mating and litter performance as well as clinical chemistry and tissue histopathology.

At 5000 ppm, liver weight in males and alkaline phosphatase in both sexes were increased. In females, after analysis of covariance, there was a decrease in ovary weights at 20,000 ppm. The only indication of reproductive toxicity was a slight decrease in implantation sites at 20,000 ppm which was likely due to reduced food intake and body weight at this dose level. Alkaline phosphatase levels were significantly increased in females at 5000 and 20,000 ppm and in males at 20,000 ppm. At 20,000 ppm total bilirubin was increased in both sexes and cholesterol levels were increased in males; albumin (and consequently total protein) was reduced in females. These clinical chemistry findings were likely the result of stress on the liver due to the high doses administered. There were no histology findings attributed to treatment and no indication of developmental toxicity at any dose level.

Under the conditions of this study, some toxicity was exhibited at levels of 5000 and 20,000 ppm, but there were no clear effects of toxicity at 1000 ppm. Therefore, the parental NOEL was considered to be 1000 ppm (100 mg/kg) while for reproductive parameters the NOEL was considered to be 5000 ppm (500 mg/kg). These data are presented in greater detail in the Robust Summaries.



### 3. Genotoxicity – *In vitro*

Genetic testing is conducted to determine the effects of substances on genetic material (i.e., DNA and chromosomes). Genetic mutations are commonly measured in bacterial and mammalian cells, and the HPV program calls for completing both types of tests. Tall oil was tested for genotoxicity in bacteria (OECD 471) and in vitro in mammalian cells (OECD 473). The genotoxicity data are summarized in Table 12 below and demonstrate that tall oil is non-genotoxic in bacterial cells and clastogenic in mammalian cells only at overtly toxic concentrations.

**Table 12**

| Chemical | Ames <i>Salmonella</i> |      | Chromosomal Aberration                             |      |
|----------|------------------------|------|--|------|
|          | +S9                    | -S9  | +S9  | -S9  |
| Tall Oil | Neg.                   | Neg. | Clastogenic<br>(at overtly toxic<br>concentration) | Neg. |

These data are presented in greater detail in the Robust Summaries.

### 4. Reproductive and Developmental Toxicity

Reproductive toxicity includes any adverse effect on fertility and reproduction, including effects on gonadal function, mating behavior, conception, and parturition. Developmental toxicity is any adverse effect induced during the period of fetal development, including structural abnormalities, altered growth and post-partum development of the offspring.

The “toxicity to reproduction” aspect of the HPV Challenge Program can be met by conducting a reproductive/developmental toxicity screening test or adding a reproductive/developmental toxicity screening test to the repeated dose study (OECD 421 or OECD 422, respectively). The reproductive/developmental toxicity data from this test on tall oil are summarized above under Repeat Dose Toxicity.

## IV. Hazard Characterization of Tall Oil and Related Substances

For potential human health effects, the totality of the SIDS data demonstrate that tall oil is non-toxic. Accordingly, based on the category approach, it can be inferred that all of the substances in this group are also non-toxic.

Tall oil has no acute oral toxicity (i.e.,  $LD_{50} > 5,000$  mg/kg), and repeat dose toxicity data demonstrate a no observed effect level (NOEL) of approximately 100 mg/kg/day. This was based on a few elevated clinical chemistry tests that were likely the result of metabolic stress on the liver at the two highest doses used. There was no evidence of reproductive or developmental toxicity in the screening test (OECD

422) conducted in conjunction with the repeat dose toxicity study with a NOEL of 500 mg/kg; the only finding of note was a decrease in implantation sites at a dose of 2000 mg/kg, which was likely due to reduced food intake and body weight deficits. The lack of acute oral toxicity (i.e.,  $LD_{50} > 2000$  mg/kg) for tall oil pitch is confirmatory of the lack of acute toxicity of the substances in this category. *In vitro* genotoxicity test results show no evidence of mutagenicity in *Salmonella* (i.e., Ames test) for tall oil. Chromosomal aberrations in Chinese hamster ovary (CHO) cells were evident only at concentrations of tall oil that were overtly toxic to the cells in the presence of metabolic activation. Consequently, no adverse health consequences would be associated with any anticipated exposures to tall oil or related substances.

With respect to potential ecotoxicological effects, the totality of SIDS data on tall oil, the representative substance in this category, demonstrate that the substances in this category are non-toxic to aquatic organisms including fish, daphnia and algae. The No Observed Effect Loading Rate (NOEL<sub>r</sub>) for tall oil fish, daphnia and alga was 1000 mg/l.

## **V. Potential Exposure to Tall Oil and Related Substances**

This brief summary provides an overview of market end uses and potential exposure to products derived from tall oil, a major feed stock to the pine chemicals industry with emphasis on tall oil and related substances. This information along with hazard data developed as part of the High Production Volume Chemical Testing Program is useful in evaluating the potential risks (if any) that might be associated with various uses of tall oil derived chemicals.

During the process of pulping coniferous trees to make paper, sodium salts of chemicals occurring naturally in the trees are produced as a co-product. When acidulated, this soap becomes tall oil. Typically, tall oil is a mixture of 25–35% rosin acids and 45–55% fatty acids with the balance being neutral compounds. Tall oil can be further processed or separated into its major components by a process of high temperature low pressure distillation. The recovery and distillation of tall oil began on a commercial scale in the mid twentieth century. As the pulp and paper industry has expanded globally so has the processing of tall oil, and the production of tall oil derivatives. At the present time there are 10 companies operating a total of 19 tall oil distillation plants in 10 countries.

Human exposure is limited by the fact that most tall oil chemicals are industrial intermediates consumed in the production of other chemicals. As such there is little, if any, potential for exposure of the general consumer population. Environmental exposure is limited by the fact that the chemical processes used in the tall oil industry are essentially closed system processes where temperature and pressure are carefully controlled.

Environmental releases from tall oil processing plants are limited to (1) treated waste water discharge, and (2) ambient emissions following treatment with scrubbers or

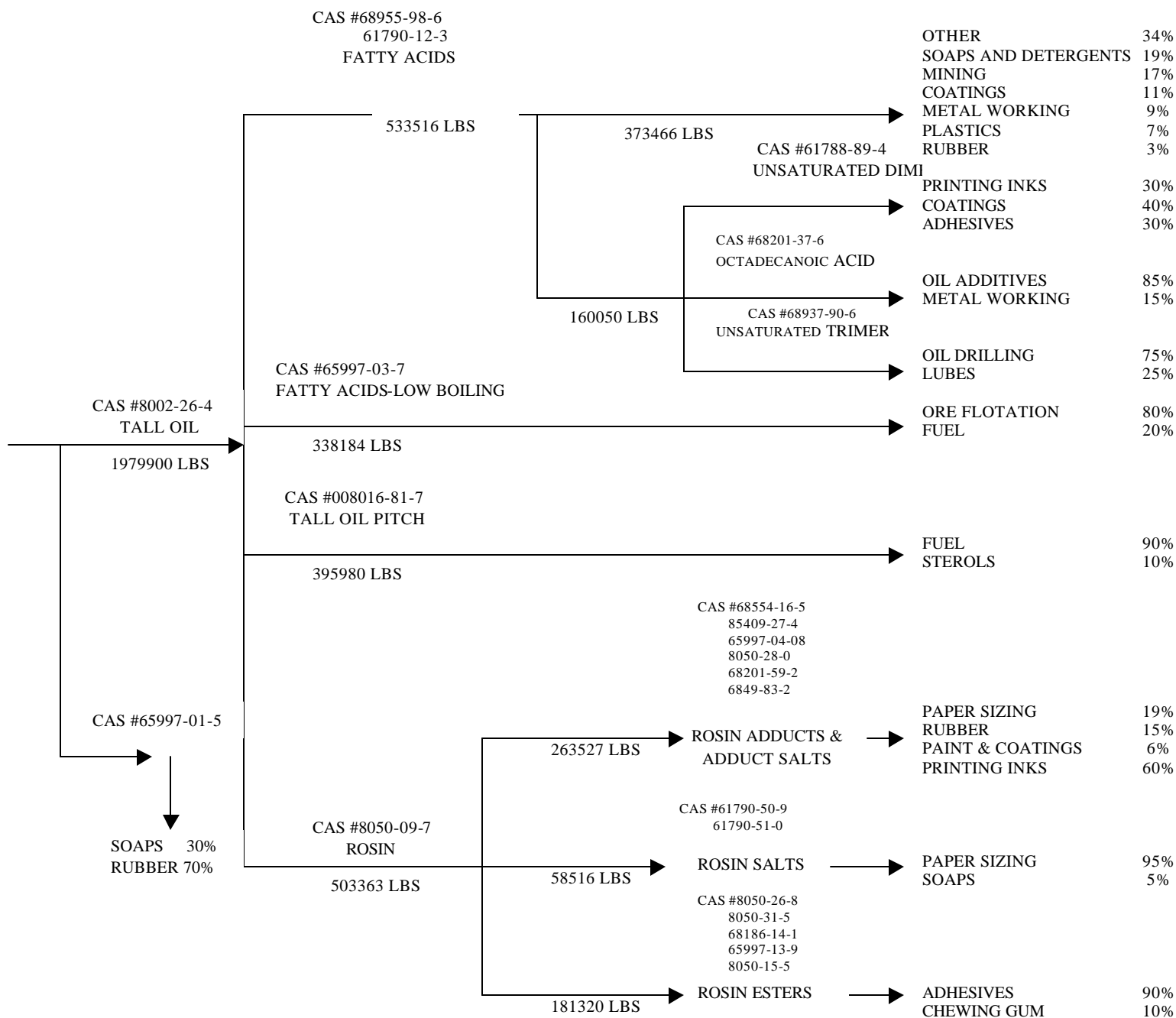
thermal oxidizers. Waste water can be generated from operation of the plant pressure control system or from minor spills and leaks associated with the process and/or handling of chemical products and routine housekeeping activities. In all cases the waste water is collected, the stream is treated to remove any free oil, and is then discharged into a larger biological waste treatment facility (either municipal treatment system or the treatment system of the paper mill). Any air emissions generated from the pressure control system or from the storage and transfer of various streams, are generally collected and treated in chemical scrubbers or thermal oxidizers.

The entire array of tall oil based chemicals and their related processing steps are best depicted by a “family tree” or flow diagram rather than a listing of discrete independent chemicals. Such a diagram demonstrates how various “parent” chemicals are consumed in the production of down stream chemicals. Consequently, it is inappropriate to sum production volumes. Figure 2 is a representation of the “family tree” for tall oil products and the relationship between these products. Based on industry data approximately 95% of tall oil is consumed during the production of other downstream products.

Table 13 illustrates general use categories and potential exposures to tall oil and related substances. Of the various tall oil products, it is estimated that greater than 95% are consumed as intermediates in the production of the wide array of products derived from tall oil. Volatilization to air and hence inhalation exposure would be minimal due to the essential lack of a vapor pressure for these substances. Exposure in all of these industrial applications is generally limited to dermal contact during manufacture of the numerous products derived from tall oil and related substances. The only other potential exposure to any of the substances in this category occurs during their production from activities such as changing reaction vessels, sampling for quality control, transferring material from one work area to another, loading and unloading bulk containers, changing filters, and cleaning equipment. The low water solubility of these compounds demonstrates that they are not bioavailable to aquatic organisms; this is confirmed by the lack of ecotoxicity to daphnia, fish and algae.

Figure 2  
U.S. TALL OIL INDUSTRY

PRODUCTION & MARKET DISTRIBUTION  
POUNDS/YEAR (000)



**Table 13**

**Distribution, Application and Potential Occupational Exposure to  
Tall Oil and Related Substances**

| <b>Substance</b>              | <b>CAS #</b>             | <b>Primary<br/>Function</b> | <b>Use Category</b> | <b>Major End Use<br/>Application</b>                | <b>%</b> |
|-------------------------------|--------------------------|-----------------------------|---------------------|---|----------|
| Tall Oil                      | 8002-26-4                | Chemical<br>intermediate    | Site limited        | Feed to<br>distillation<br>Derivative<br>production | 95<br>5  |
| Tall Oil, Salts               | 65997-01-5<br>68647-71-2 | Chemical<br>intermediate    | Industrial          | Soaps   | 100      |
| Tall Oil<br>Disproportionated | 068152-92-<br>1          | Processing aid              | Industrial          | Rubber  | 100      |
| Tall Oil Pitch                | 008016-81-<br>7          | Chemical<br>intermediate    | Site limited        | Fuel  | 90       |

## References

EPA. 2000. Data Collection and Development on High Production Volume (HPV) Chemicals. Fed. Reg. Dec. 26, Vol. 65(248): pp. 81686-81698.

Zinkel, D.F. and Russell, J., Eds. 1989. Naval Stores. Production, Chemistry, Utilization. Pulp Chemicals Association, New York.

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